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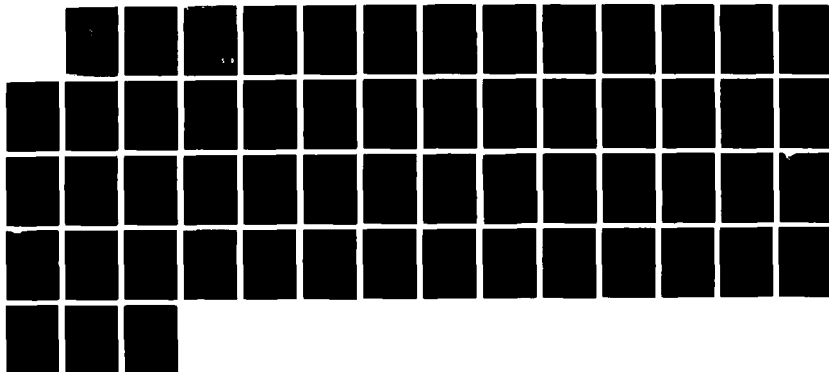
THEORETICAL STUDIES OF SOLIDS UNDER EXTREME CONDITIONS
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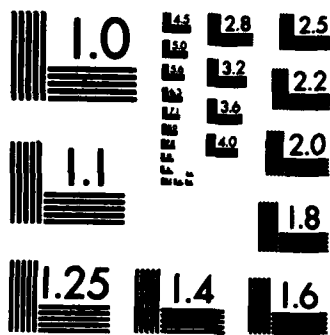
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TO

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"THEORETICAL STUDIES OF SOLIDS UNDER EXTREME CONDITIONS"

APRIL 1987

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Ab Initio SCF Calculations on the Molecules

Nitrosamine and Nitrosamine

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Ab Initio SCF Calculations on the Molecules

Nitroamine and Nitrosamine

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Abstract

The electronic structures of the molecules nitroamine and nitrosamine have been investigated by using ab initio molecular orbital methods. Double-zeta basis sets have been used. Both planar and non-planar geometries have been considered and complete geometry optimizations have been performed. The results obtained are compared with previous semi-empirical and ab initio studies.

1. Introduction

Nitramine and nitrosamine compounds are of significant interest (Feuer et al. 1969) due to their extensive use as essential ingredients in propellants and primary and secondary explosives. X-ray crystallographic studies of these compounds in conjunction with microwave and electron diffraction studies indicate that these molecules exhibit a number of interesting geometrical features. For nitramine, apart from the study by Beavers et al. (1957) the most exhaustive study is that of Tyler (1963) where the non-planarity of nitramine is shown by the direct observation of the NH_2 inversion. However, there continue to be different (Gropen and Skancke 1971, Cimiraglia 1978) studies on the contrary, and the fact that dimethyl-nitramine is planar (Stolevik and Rademacher 1967) illustrates the necessity of further theoretical and experimental work for the accurate determination of the electronic structures.

The aim of the present work is, therefore, to study the optimized geometries of nitramine and nitrosamine in both planar and non-planar form, at the Hartree-Fock level. The non-planar form of nitramine will be taken from the study of Tyler and the planar forms of both the molecules will be taken from the study of Gropen et al (1971). Our results will be compared with a number of semi-empirical studies (Farminer and Webb 1975, Harris 1973, White, Colton, Lee and Rabalais 1975).

2. Details of Calculations

As is well known, the ab initio molecular-orbital method predicts geometries with surprising accuracy, in spite of the neglect of correlation energy. However, there appears to be only two ab initio studies in the literature for these molecules. The study by Gropen et al. (1971) considered only planar geometry and no geometry optimization was performed. The study by Duke (1978) used minimum basis sets and only partial geometry optimization was performed. The NO_2 and NH_2 geometries were kept fixed; only the N-N distance and the out-of-plane angle of the NH_2 group were varied.

To improve these results, we have used a double-zeta basis set, namely the 3-21G basis set (Binkley, Pople and Hehre 1980). This basis consists of an s-type inner shell function with 3 Gaussians, an inner set of valence s- and p- type functions with 2 Gaussians and another outer sp set with 1 Gaussian. This basis should give reasonable bond angles and bond lengths, which are known to be overestimated in a minimal basis-set study. Geometry optimization was performed by using the method of Schlegel (1982). This optimization algorithm evaluates and utilizes the gradients each time the energy is computed and the second derivative matrix is updated. This is followed by a one-dimensional search using the second derivative matrix.

3. Results and Discussion

The results obtained are presented in Tables 1 - 12.

In Tables 1 and 2, the non-planar experimental geometries of nitramine and the optimized geometry at the Hartree-Fock 3-21G level are presented. The N-N distance obtained, 1.472 Å, is, not surprisingly, too large. This is to be compared with the N-N distance, 1.354 Å, obtained at planar geometry. Obviously, there is a strong tendency to planarity at shorter N-N distances. MINDO predicts nitramine to be a planar molecule, MINDO2 gives 1.21 Å for N-N distance, while MINDO3 gives 1.29 Å.

In tables 3 and 5, we present the calculated orbital energies for nitramine in non-planar and planar forms. The nature of each orbital is indicated in terms of π -bonds and more or less localized σ bonds. The four lowest occupied orbitals are the inner shell s-orbitals on the four heavy atoms. This feature is also supported by the MINDO2 and MINDO3 orbital energies. The photoelectron spectrum of nitramine indicates that the two highest occupied levels are of π symmetry. Our calculations indicate that while this is true for planar nitramine, in non-planar nitramine, only the highest occupied level is of π symmetry. Also, in the study by Gropen et al., one lone pair is found between the two σ (N-H) orbitals and the lowest π orbital was found to be almost degenerate with the highest of these. We do not observe such degeneracy and thus it seems unlikely that the lowest π orbital is almost completely delocalized as has been claimed in the literature.

In Tables 6 and 7, the optimized planar geometry and the orbital energies for nitrosamine are presented. Here the three lowest orbitals are the inner shell s-orbitals on the three heavy atoms. A study of population analysis indicate complete agreement with the conclusions reached by Gropen et al.: the three highest occupied σ orbitals are responsible for the lone pairs on nitrogen and oxygen. Also, the two lowest, 5a' and 4a', are mainly responsible for the σ (N-O) and σ (N-N) bonds.

Table 8 contains the results of the total energies, before and after optimization. Since nitramine in planar form has clearly lower energy than nitramine in non-planar form and since experimental study by Tyler (1963) indicate results on the contrary, further experimental research in this direction could be very fruitful.

Table 9, 10, and 11 present the results of gross atomic population study. In the non-planar form, the nitro nitrogen atom is positively charged, namely +0.51 while the amine nitrogen atom is negatively charged, namely -0.51. This is from Mulliken population analysis. Results from Lowdin population analysis indicate that the nitro nitrogen atom is positively charged, +0.46 but the amine nitrogen is strongly negatively charged, namely -0.71. The same qualitative trends are predicted from the CNDO charges which are in reasonable agreement with the INDO charges reported by White (1975). It is interesting to note that for nitramine in planar form, the conclusions are completely opposite. We note as a sideline that MINDO methods do not work very well in the study of the population charges of these molecules, probably because these molecules are very different from those used in

the parameterisation of such methods. It is also to be remembered that the predicted populations in any ab initio calculation are very sensitive to the choice of basis set.

Finally in Table 12, we compare our results for the dipole moment of nitramine with the available results in the literature. In the non-planar form, our value for the dipole moment is the closest to the experimental value. However, since total energy is considered more reliable in ab initio method, nitramine in planar form still appears to be more stable theoretically. Again, further experimental work would be very welcome.

ACKNOWLEDGEMENTS

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TABLE 1

Experimental bond lengths and bond angles for nitramine (lengths in nm)

	Beevers and Trotman-Dickinson (1957) X-ray	Tyler (1963) Microwave
N-H		0.1005 ± 0.001
N-H	0.140	0.1427 ± 0.0002
N-O	0.118	0.1206 (assumed)
ONO		$130^{\circ}8' \pm 15'$
HNH		$115^{\circ}11' \pm 2^{\circ}$
out of plane		$51^{\circ}47' \pm 1^{\circ}$

TABLE 2

Optimized Non-planar Geometry of Nitramine Coordinates are in Angstroms.

Atom	x	y	z
N(1)	0.0145	-0.0021	0.0
N(2)	1.4845	0.0754	0.0
O(1)	-0.5963	1.0803	0.0
O(2)	-0.4676	-1.1209	0.0
H(1)	1.7172	0.6055	0.8295
H(2)	1.7172	0.6055	-0.8295

TABLE 3

Orbital energies for nitroamine in a. u.

Orbital	Orbital energy	Nature of Orbital
1 (1a')	-20.531190	1s
2 (2a')	-20.511603	1s
3 (3a')	-15.810688	1s
4 (4a')	-15.574496	1s
5 (5a')	- 1.631171	σ
6 (6a')	- 1.424051	σ
7 (7a')	- 1.261226	σ
8 (8a')	- 0.905639	σ
9 (1a'')	- 0.786352	π
10 (9a')	- 0.775029	σ
11 (10a')	- 0.723289	σ
12 (2a'')	- 0.665820	π
13 (11a')	- 0.538030	σ
14 (12a')	- 0.499191	σ
15 (13a')	- 0.467081	σ
16 (3a'')	- 0.443007	π

TABLE 4

Initial and Optimized Planar Geometries of Nitramine Coordinates are in Angstroms.

Atom	x_{in}	y_{in}	x_{opt}	y_{opt}
N(1)	0.0	0.0	0.0	-0.0065
N(2)	0.0	1.3816	0.0	1.3476
O(1)	1.0926	1.8911	1.1170	1.9019
O(2)	-1.0926	1.8911	-1.1170	1.9019
H(1)	0.8474	-0.5398	0.8937	-0.4426
H(2)	-0.8474	-0.5398	-0.8937	-0.4426

TABLE 5

Optimized Orbital Energies for nitramine in planar form in a.u.

Orbital	Orbital energy	Nature of Orbital
1 (1a')	-20.495737	1s
2 (2a')	-20.495366	1s
3 (3a')	-15.814295	1s
4 (4a')	-15.580724	1s
5 (5a')	- 1.617184	σ
6 (6a')	- 1.401714	σ
7 (7a')	- 1.282449	σ
8 (8a')	- 0.924754	σ
9 (9a')	- 0.799121	σ
10 (10a')	- 0.769095	σ
11 (1a'')	- 0.746520	π
12 (11a')	- 0.671962	σ
13 (12a')	- 0.497412	σ
14 (13a')	- 0.482884	σ
15 (2a'')	- 0.472506	π
16 (3a'')	- 0.437638	π

TABLE 6

Initial and Optimized Planar Geometries of Nitrosamine. Coordinates are in Angstroms.

Atom	x_{in}	y_{in}	x_{opt}	y_{opt}
N(1)	0.0	0.0	0.0060	-0.0062
N(2)	0.0	1.3436	-0.0164	1.3413
O(1)	1.0926	1.8531	1.1001	1.8513
H(1)	0.8474	-0.5398	0.8896	-0.4737
H(2)	-0.8474	-0.5398	-0.8690	-0.4746

TABLE 7

Optimized Orbital Energies for nitrosamine in a. u.

Orbital	Orbital Energy	Nature of Orbital
1 (1a')	-20.489050	1s
2 (2a')	-15.659971	1s
3 (3a')	-15.546273	1s
4 (4a')	- 1.523223	σ
5 (5a')	- 1.248262	σ
6 (6a')	- 0.915149	σ
7 (7a')	- 0.770635	σ
8 (8a')	- 0.696589	σ
9 (1a'')	- 0.623923	π
10 (9a')	- 0.586597	σ
11 (2a'')	- 0.424889	π
12 (10a')	- 0.414389	σ

TABLE 8

Total electronic energies. Values in a. u.

Molecule	Geometry	Total Energy
Nitramine	Non-Planar (Expt.)	-258.004191
	Non-Planar (Opt.)	-258.118307
Nitramine	Planar (Theo.)	-258.128685
	Planar (Opt.)	-258.137938
Nitrosamine	Planar (Theo.)	-183.764893
	Planar (Opt.)	-183.768075

TABLE 9

Gross atomic population for nitramine in non-planar geometry.

Atom	Total Charge (Mulliken)	Total Charge (Lowdin)
N(1)	6.49297	6.54222
N(2)	7.51055	7.29311
O(1)	8.39306	8.33289
O(2)	8.33329	8.24663
H(1)	0.63507	0.79258
H(2)	0.63507	0.79258

TABLE 10

Gross atomic population for nitramine in planar geometry.

Atom	Total Charge (Mulliken)	Total Charge (Lowdin)
N(1)	7.55396	7.29915
N(2)	6.45242	6.48963
O(1)	8.40378	8.34106
O(2)	8.40378	8.34106
H(1)	0.59033	0.76455
H(2)	0.59033	0.76455

TABLE 11

Gross atomic population for nitrosamine in planar geometry.

Atom	Total Charge (Mulliken)	Total Charge (Lowdin)
N(1)	7.62222	7.31078
N(2)	6.71360	6.81728
O(1)	8.41915	8.29476
H(1)	0.62775	0.79472
H(2)	0.61729	0.78245

TABLE 12

Comparison of dipole moments of nitramine.

Method	Nitramine
CNDO (Duke 1978)	4.44
MINDO3 (Duke 1978)	3.95
INDO (Whitman and Hornback 1969)	4.12
Ab initio (Gropen et al. 1971)	4.42
Ab initio (Duke 1978)	3.75
This work (non-planar)	3.62
This work (planar)	4.66
Exp.	3.57

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A recommendation for the increased use
of artificial intelligence programming in physics

by

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A recommendation for the increased use
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ABSTRACT

The recent availability of artificial intelligence programs and Lisp machines brings a completely new class of computing tools to the physicist. In this paper we try to provide a pedagogical introduction to this not so common class of computing by demonstrating some of the general applications of these programs, by showing one of its applications in solid state physics research, and by suggesting other research and classroom applications.

I. INTRODUCTION

During the past decade the use of digital computers has become an integral part of research in solid state physics. In most cases the uses of computers have been primarily either for numerical calculations or for control, data acquisition, and data analysis in experiments. In this paper we try to point out a different type of use, namely for algebraic (or symbolic) manipulation. This type of computer programming is part of a larger field which is known as artificial intelligence and is expected to make a very large impact in the next generation of computers.

Although a number of researchers in physics have used computers for algebraic programming, it is still an unfamiliar topic to a large fraction of physics faculty and students. Thus in the first part of this paper we take a pedagogical approach and introduce the use of algebraic programming via examples. In subsequent parts we present its application to a particular problem in solid state physics, namely the formulation of band structure calculations based upon the linear combination of atomic orbitals (LCAO) method. The examples presented in the rest of the paper are based on the "computer language" REDUCE.¹ The easy availability of this language over the more powerful ones, like MACSYMA,² was the reason for this choice.

II. ALGEBRAIC PROGRAMMING

The primary purpose of algebraic manipulation programs is to process formal mathematical expressions, without any particular concern for their numerical values. Basically these expressions are processed in a fashion similar to the one used in an algebra or calculus class. Since almost all of the readers of this paper are familiar with numerical programming using computer languages like BASIC or FORTRAN, we think it is most instructive to present an example comparing the algebraic programming method with the numerical programming method.

Example I

Let us consider the expression

$$(X^2 - Y^2) / (X+Y). \quad (1)$$

If we write a FORTRAN program as

$$Z = (X**2 - Y**2) / (X+Y) \quad (2)$$

$$\text{PRINT } (5,*) \text{ } Z \quad (3)$$

$$\text{END} \quad (4)$$

and execute it, the result will be completely meaningless and some compilers will warn that the X and Y variables are "undefined." Running a similar program from a BASIC interpreter will produce a similar error message. If we run a program in REDUCE as

$$Z := (X**2 - Y**2) / (X+Y); \quad (5)$$

the result will be $(X - Y)$.

The main difference between the two types of programming is illustrated in the above example. In the numerical programming method, one must assign a numerical value to each variable before an expression containing it is evaluated, whereas in algebraic programming one obtains an answer which is true for all different values of the variables. Since in solid state physics problems, as well as in a number of other branches of science, one needs to translate a physical model into mathematical expressions before starting numerical programming, in most of these cases the algebraic programming method could be used to obtain those expressions. In table I we have presented a few examples using REDUCE. On one line the operation is defined, followed by a semicolon. On the lines after the semicolon the results from the execution of REDUCE are printed. Examples of differentiation and integration are given. The statements starting with ON or OFF are control directives to the REDUCE program and may be ignored during the reading of this paper without loss of understanding. The computer used for these examples was a DEC 2060 running with the TOPS-20 operating system, but these examples can be run in any implementation of REDUCE yielding the same results.

III. LCAO BANDSTRUCTURE

In this section, as a specific application, we present the use of REDUCE in obtaining the expressions for the linear combination of atomic orbitals (LCAO) Hamiltonian matrix elements for electrons in a crystal. An introduction to the band theory in general and the LCAO method in particular can be obtained from many solid state physics texts.³ Also, the original paper by Slater and Koster,⁴ and a review article by Nussbaum,⁵ contain a comprehensive discussion of the theory involved. In light of this, a detailed introduction will be omitted here. This method has been a very effective starting point for the study of defects,⁶ surfaces,⁷ the electron-phonon interaction,⁸ and Fermi-surface properties.⁹

In the LCAO formulation of the band structure problem, one expresses the conduction electron wave function $\psi_{n\vec{k}}(\vec{r})$ as a linear combination of atomic orbitals (hence the name LCAO):

$$\psi_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{mj} c_{jn} e^{i\vec{k} \cdot \vec{R}_m} \phi_{jm}(\vec{r}) \quad (6)$$

where $\phi_{jm}(\vec{r})$ is the atomic orbital centered at site m and the summation j runs over all the atomic orbitals considered, e.g. orbitals of symmetry s, x, y, xy, yz , etc. The energy levels and wave functions for the electrons are obtained by diagonalizing the matrix H_{ij} , where

$$H_{ij} = \frac{1}{N} \sum_{\mathbf{m}, \mathbf{m}'} e^{i\mathbf{k} \cdot (\mathbf{R}_m - \mathbf{R}_{m'})} \langle \phi_{im} | H | \phi_{jm'} \rangle \quad (7)$$

and H is the Hamiltonian. The above expression for H_{ij} , after a commonly-used approximation called the two center approximation^{4,5} can be written as

$$H_{ij} = \sum_{p(\text{neighbors})} e^{i\mathbf{k} \cdot \mathbf{R}_p} E_{ij}(\mathbf{R}_p) \quad (8)$$

where \mathbf{R}_p represents the lattice sites and E_{ij} is a unique function of i , j , and \mathbf{R}_p . The functional dependence of E_{ij} on \mathbf{R}_p can be further subdivided into radial and angular parts. The E_{ij} expressions for a few different values of i and j are:

$$E_{sx} = \lambda(sp\sigma) \quad (9)$$

$$E_{s,x^2-y^2} = \sqrt{3}/2(\lambda^2 - m^2)(sd\sigma) \quad (10)$$

$$E_{x,3z^2-r^2} = \lambda(n^2 - (\lambda^2 + m^2)/2)(pd\sigma) - \sqrt{3}mn^2(pd\pi) \quad (11)$$

where λ , m , and n are the direction cosines of \mathbf{R}_p , representing the angular part, and $(ss\sigma)$, $(pp\pi)$, etc. are two-centered bond parameters, representing the radial part. A complete list of the functions is given in references 4 and 5. A general procedure, which can also be implemented using REDUCE, is given by Sharma.¹⁰

In evaluating H_{ij} , the contribution from the radial part is usually determined from numerical calculations or from a

parametric fit, and that from the angular part is obtained by analytically summing over the \vec{R}_p . As an example, we will consider the contribution to H_{sx} for the nearest neighbors in a body-centered cubic (bcc) lattice. The number of nearest neighbors in this case is eight and their coordinates and $(l \ m \ n)$ values are listed in Table II. Substituting these values of $(l \ m \ n)$ and the form of E_{sx} from equation 9 into equation 8, one gets

$$H_{sx} = 2i \sin(k_x a)(sp\sigma) , \quad (12)$$

where a is the lattice constant. This expression is the contribution of the nearest neighbors in a bcc lattice to H_{sx} . Although the contributions from other matrix elements, and for different lattices can be obtained in an identical fashion, the process is extremely tedious, error-prone, and time consuming. Table III contains a program in REDUCE which evaluates the sum over \vec{R}_p , given the \vec{R}_p vectors. Readers interested in getting a feel for the advantage of using this program may try evaluating one of the d-d matrix elements, or may look in Ref. 4 or 5 at the complicated results for s, p, and d orbital symmetries. Readers not familiar with the programming language REDUCE should only be concerned with the remarkable brevity of a program which yields the complicated LCAO expressions for arbitrary angular momentum orbital basis functions.

IV. OTHER APPLICATIONS

Artificial intelligence programming has countless applications. These applications include complicated integrations, differentiations, limit evaluations, summations, and application of recursion relations to give analytic expressions. These programs are very efficient in performing the more tedious kinds of operations in which humans have a high rate of error.

Since most students in physics as well as the other sciences are acquainted with personal computers and mainframe computers, and use them in both graduate and undergraduate studies, an introduction to artificial intelligence programming at an early stage in the student's career is now appropriate. This can be done in many physics classes, but certainly in courses in mathematical methods of physics at any level.

A few other examples of useful REDUCE programs are programs which produce explicit expressions for the following:

- 1) orthogonal polynomials of arbitrary order
- 2) spherical harmonics of arbitrary l and m
- 3) spherical Bessel functions of arbitrary order
- 4) Clebsch-Gordon coefficients.

A comment on the last item is informative and illustrative of the power of REDUCE. Many man-years of effort have been expended in computing Clebsch-Gordon coefficients of high order. Numerical calculations are difficult because of factorial functions of large arguments. Extensive tables of the coefficients have been

published, both in prime number representation and decimal representation. Using REDUCE we have written a simple program which very quickly gives an analytic expression for or a numerical value of the coefficient for arbitrary angular momenta without any of the computational difficulties encountered in previous methods.¹¹

V. CONCLUSION

We have demonstrated the utility of algebraic programming by presenting a specific example of how it has been used in solid state physics research.¹² The advantages of this method are threefold. First, the tedium of deriving many expressions using the same method is greatly reduced. Second, a great deal of time can be saved by using the computer to do repetitive derivations. Finally, the chances of error in the derivations and in transcription of the equations are minimized. The latter is due to the fact that REDUCE has the capability of writing the results in FORTRAN.

With the recent stress on artificial intelligence and fifth generation computers, there is a growing need for more researchers and students to become familiar with programming languages like REDUCE. Not only are they useful, they may soon become a necessary part of any scientific researcher's tools. Artificial intelligence may remove the bottleneck between the conception of a solution to a problem and its execution, giving the student and researcher more time to think and learn, as well as the ability to attack problems of greater complexity.

We are convinced that in the future the use of artificial intelligence programs will be just as important a part of training for scientists as learning how to read a voltmeter or use a microscope.

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Table Captions

Table I. Examples of the use of REDUCE for differentiation and integration of selected functions.

Table II. Nearest-neighbor positions and direction cosines for the BCC lattice. The nearest-neighbor distances have been multiplied by $2/a$, where a is the lattice constant, and the direction cosines have been multiplied by $\sqrt{3}$.

Table III. A REDUCE program which was used for the evaluation of Slater-Koster matrix elements.

Table I

COMMENT The following are examples of differentiation:

The syntax is DF(F , X , n),
where function F is differentiated n times with respect
to the variable X;

DF(X**3 , X , 1);

$$3 * X^2$$

DF(X**N * SIN(X) , X , 2);

$$(X^N * (2 * \cos(X) * X^N - \sin(X) * X^2 + \sin(X) * N^2 - \sin(X) * N)) / X^2$$

DF(X**(X**X) , X , 3);

$$\begin{aligned} & (X^X + X) * (X^{(2*X)} * \log(X)^6 * X^3 + 3 * X^{(2*X)} * \log(X)^5 * X^3 + 3 * X^{(2*X)} * \\ & \log(X)^4 * X^3 + 3 * X^{(2*X)} * \log(X)^4 * X^2 + X^{(2*X)} * \log(X)^3 * X^3 + \\ & 6 * X^{(2*X)} * \log(X)^3 * X^2 + 3 * X^{(2*X)} * \log(X)^2 * X^2 + 3 * X^{(2*X)} * \\ & \log(X)^2 * X + 3 * X^{(2*X)} * \log(X) * X + X^{(2*X)} * X^5 + 3 * X^X * \log(X)^5 * \\ & X^3 + 9 * X^X * \log(X)^4 * X^3 + 9 * X^X * \log(X)^3 * X^3 + 12 * X^X * \log(X)^3 * \\ & X^2 + 3 * X^X * \log(X)^2 * X^3 + 21 * X^X * \log(X)^2 * X^2 - 3 * X^X * \log(X)^2 * \\ & X + 9 * X^X * \log(X)^2 * X^2 + 6 * X^X * \log(X)^2 * X + 6 * X^X * X^5 - 3 * X^X * \\ & \log(X)^4 * X^3 + 3 * \log(X)^3 * X^3 + 3 * \log(X)^2 * X^3 + 6 * \log(X)^2 * X^2 \\ & + \log(X)^3 * X^3 + 9 * \log(X)^2 * X^2 - 4 * \log(X) * X + 3 * X^2 + 2)) / X^3 \end{aligned}$$

DF(A*X * ASIN(X) , X , 2);

$$(\sqrt{X^2 - 1} * A * I * (-X^2 + 2)) / (X^4 - 2 * X^2 + 1)$$

Table I (continued)

COMMENT The following are examples of integration.

The syntax is $\text{INT}(F, X)$,
where F is the integrand and X is the variable of
integration.;

$\text{INT}(1/X, X);$

$\text{LOG}(X)$

$\text{INT}(X^P * \text{LOG}(X), X);$

$(X^P * X * (\text{LOG}(X)^P + \text{LOG}(X) - 1)) / (P^2 + 2P + 1)$

$\text{INT}(\text{SIN LOG } Q, Q);$

$(Q * (-\text{COS}(\text{LOG}(Q)) + \text{SIN}(\text{LOG}(Q)))) / 2$

$\text{INT}(A^X, X);$

$A^X / \text{LOG}(A)$

$\text{INT}(A^X * \text{SIN } X, X);$

$(A^X * (\text{LOG}(A) * \text{SIN}(X) - \text{COS}(X))) / (\text{LOG}(A)^2 + 1)$

$\text{INT}(X * \text{ATAN } X, X);$

$(\text{ATAN}(X)^2 * X + \text{ATAN}(X) - X) / 2$

Table II

BCC Lattice

Nearest-neighbor position ($\times 2/a$)Direction cosines ($\times \sqrt{3}$)

<u>X</u>	<u>Y</u>	<u>Z</u>	<u>l</u>	<u>m</u>	<u>n</u>
1	1	1	1	1	1
-1	1	1	-1	1	1
1	-1	1	1	-1	1
-1	-1	1	-1	-1	1
1	1	-1	1	1	-1
-1	1	-1	-1	1	-1
1	-1	-1	1	-1	-1
-1	-1	-1	-1	-1	-1

Table III

Comment This program derives the equation for TB bandstructure;

OFF NERO; OFF ECHO;

Comment Read in the $E(l,m,n)$ s and the R vectors;

IN "ELMN.RED"\$ IN "RVEC.RED"\$

FOR ALL X LET $EX(X) = \cos(X) + I \cdot \sin(X)$;
 FOR ALL X,Y LET $\cos(X+Y) = \cos(X) \cdot \cos(Y) - \sin(X) \cdot \sin(Y)$;
 FOR ALL X,Y LET $\sin(X+Y) = \sin(X) \cdot \cos(Y) + \cos(X) \cdot \sin(Y)$;
 LET $A \cdot K1 = XI$; LET $A \cdot K2 = ETA$; LET $A \cdot K3 = ZETA$;
 FACTOR I;

Comment IV represents different types of integral, e.g (s/x) ;

FOR IV:=1:29 DO BEGIN E(IV);
 WRITE " TYPE =" ,IV;

Comment Sum over the R vectors;

FOR J := 1:26 DO BEGIN
 IF ((J=1) OR (J=7) OR (J=19)) THEN V := 0;
 RL := 0;
 FOR J1 := 1:3 DO RL := RL + R(J1,J) * R(J1,J);
 RL := RL ** (1/2) ;
 L := R(1,J) / RL ; M := R(2,J)/RL; N:= R(3,J)/RL;
 V := V + EX(K1 * R(1,J) + K2 * R(2,J) + K3 * R(3,J)) ;
 IF ((J=6) OR (J=18) OR (J=26)) THEN WRITE " H(I,J) = ", V;
 END;
 END;
 END;

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A Configuration Interaction Study of Small Lithium Clusters

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Abstract

A detailed study of Li_2 , Li_3 and Li_4 clusters is reported at the ab initio level. Fourteen different geometries of the clusters have been considered. The most stable geometrical forms at the Hartree-Fock-Configuration-Interaction level are found and compared with previously published theoretical and experimental results.

I. Introduction

In recent years, there has been widespread interest in theoretical investigation of metal clusters (Schaefer 1975). The understanding of the properties of small clusters is of signal importance in many areas, particularly dispersed metal catalysis. Lithium, as the simplest metal, has been the subject of many of these studies (Stoll and Preuss 1972, Marshall, Blint and Kunz 1976, Borisov 1976, Gerber and Schumacher 1978, Hermann and Bagus 1978, Beckmann et al. 1979) primarily because simple quantum chemical methods as well as sophisticated self-consistent-field methods can be employed for evident reasons. As a result, a number of results of different quality on different clusters is now available. For example, *ab initio* Self-Consistent-Field (Davies and Del Conde 1976), Configuration Interaction (Kress, Carberry and Kuczynski 1978), Coupled-Electron-Pair-Approximation (Meyer 1977) and Diatomics-In-Molecules (Companion, Steible and Starshak 1968) studies of Li clusters have been published but the obtained results are hardly in agreement with each other. In this study and the studies to follow, we want to use one method only, namely Hartree-Fock followed by full configuration interaction in the entire spectrum of diatomic molecule to very large clusters. The ultimate aim is to determine precisely what size and shape of the cluster which can be used, to a reasonable approximation, to simulate the effects of the infinite solid. This work concentrating on small Li_2 , Li_3 and Li_4 clusters is the first one in a series of exhaustive study of metal clusters at the Hartree-Fock-Configuration-Interaction level. It is hoped that such a consistent study will help resolve the controversies surrounding the size, shape and stability of small Li clusters.

II. Geometry of Clusters

Clusters investigated in this work are taken from different studies available in the literature and are shown in Fig. 1. Triangular, equidistant and general Li_3 clusters are investigated. The parameters are taken from a comparable CNDO/BW (Complete Neglect of Differential Overlap) study (Skala 1981) since it is known that such parameterization is able to give the quantities of primary interest, i.e. bond lengths, bond angles and binding energies to a fairly good accuracy (Boyd and Whitehead 1981). Of course, it is expected that a HF followed by CI calculation will improve the results of semiempirical studies considerably. Ten different structures of Li_4 are taken into account: tetrahedral (tet), triangular (tri), square (sq), linear equidistant (eq), linear consisting of two diatomic molecules (mol), general linear (lin), oblong formed by two parallel diatomic molecules (obl), T-shaped (T), rhombic formed by two diatomic molecules (rho) and parallelepiped (para).

III. Computational Method

One of the primary considerations involved is determination of the type of basis set to be used. Gaussian-type basis sets used in ab initio molecular orbital computations usually involve some compromise between computational cost and accuracy. A considerable increase in computational efficiency can be achieved if the exponents of the Gaussian primitives are shared between different basis functions. At the split-valence level, this is usually exploited by sharing primitive exponents between s and p functions for the valence functions. Accordingly, for lithium, we have

used here the so-called 3-21 G basis set (Binkley, Pople and Mehre 1980). This basis consists of s-type inner shell function with 3 Gaussians, an inner set of valence s- and p-type functions with 2 Gaussians and another outer sp set with 1 Gaussian.

Once the basis set has been decided upon, Hartree-Fock calculations have been carried out followed by full CI involving all single and double excitations. The use of the method of configuration interaction is crucial since it is well known (Das 1967) that conventional Hartree-Fock methods do not describe Li_n systems accurately. These CI calculations have been performed within the framework of the Graphical Unitary Group Approach (GUGA-CI) of Brooks and Schaefer (1979). It is to be noted that GUGA-CI approach is computationally well tractable compared to conventional CI methods.

IV. Results

The results of our calculations are presented in Tables 1 and 2. The parameters are listed in Column 2 of Table 1. ΔE indicates the energy separation between the lowest unoccupied molecular orbital and the highest occupied molecular orbital and E_{tot} is the total energy, i.e. the core repulsion energy plus the valence electron energy. E_b is the binding energy per atom given by

$$E_b = (NE_{\text{Li}} - E_{\text{Li}_N})/N \quad (1)$$

where N is the number of atoms in the cluster. Table 2 lists the first and the second ionization potentials. The first ionization potential is obtained from Koopman's theorem

$$\text{I. P.} = -E_{\text{homo}} \quad (2)$$

and the second ionization potential was obtained from the orbital below the highest occupied molecular orbital.

For Li_2 , the separation distance was taken to be the equilibrium experimental separation. Our value for the first ionization potential 4.89 eV compares favorably with the experimental ionization potential 4.96 eV. The difference could be attributed to the basis set. The CI was fairly small, involving only 553 configurations, counting all single and double excitations.

For Li_3 , the conclusions agree with the results of Skala (1981) and Kendrick and Hillier (1977) at the Hartree-Fock level. This implies that at this ab initio level, the most stable Li_3 cluster has the form of a non-equilateral triangle. The total energy of linear equidistant Li_3 is found to be lower than that of the triangular Li_3 . This agrees with the results of Skala (1981) and Companion (1978) but in contrast to the results of Kendrick et al. (1977).

The results of the binding energy calculations indicate also that Li_3^{iso} should be unstable. This contradicts the experimental results of Wu (1976); however, other recent experimental works indicate that clusters with odd number of atoms are less probable than those with even number of atoms. The origin of this discrepancy could also be due to the parametrization method inherent in the CNDO/BW approximation, as correctly observed by Skala (1981).

The Li_4 results are probably the most exhaustive ab initio study on this system. The CI in these cases were fairly large, typically 11000 configurations counting all single and double excitations. At the Hartree-Fock-Configuration-Interaction level, the binding energy increases along the following sequence of geometries: tetrahedral, oblong, triangular,

square, linear equidistant, molecular, T-shaped, rhombic and parallelopiped. The CNDO/BW study of Skala (1981) with the same parameters found the following sequence of geometries: tetrahedral, triangular, square, equidistant, molecular, linear, oblong, T-shaped, rhombic and parallelopiped. Other works on Li_4 usually take into account only two or three geometries and the most stable system is that of square form (Companion 1978). There is however no contradiction, since Li_4^{rho} or $\text{Li}_4^{\text{para}}$ were not considered. The binding energy $2E_{\text{tot}}(\text{Li}_2) - E_{\text{tot}}(\text{Li}_4^{\text{para}})$ is found to be 0.495 eV, to be compared with the result 0.956 eV of Skala (1981) and 0.668 eV of Companion (1978).

Finally, the result of the dipole moment calculations show that except for Li_3^{iso} , Li_4^{mol} , Li_4^{T} and $\text{Li}_4^{\text{para}}$, the dipole moment equals zero. Since most stable Li_n systems should have nonzero dipole moment, experimental determination of dipole moments can help determine the cluster geometries.

ACKNOWLEDGEMENTS

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Fig. 1. Geometry of two-, three-, and four- atomic clusters

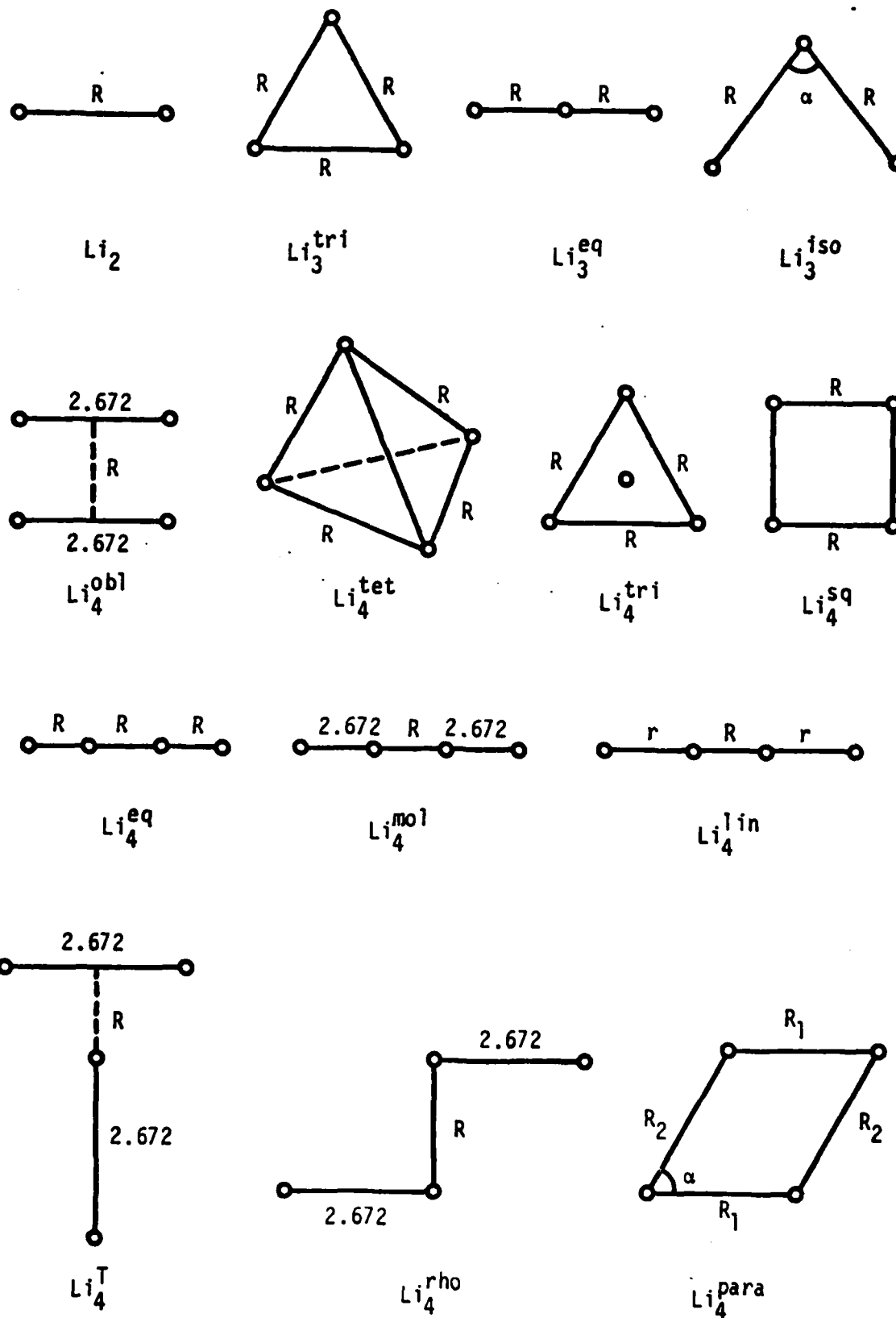


Table 1. The values of the geometrical parameters, the homo-lumo gaps ΔE , the total energy E_{tot} in a.u., the binding energy per atom E_b in a.u., and the dipole moment in Debye.

Cluster	R	ΔE	E_{tot}	E_b	D
Li_2	2.672	0.1903	-14.7966	0.0168	0.0
Li_3^{tri}	2.96	0.0431	-22.1654	0.0070	0.0
Li_3^{eq}	2.75	0.0938	-22.1696	0.0084	0.0
Li_3^{iso}	$R=2.82$ $\alpha=72.2^\circ$	0.0674	-22.1735	0.0097	0.375
Li_4^{tet}	3.01	0.1213	-29.5773	0.0128	0.0
Li_4^{tri}	3.89	0.1218	-29.5874	0.0151	0.0
Li_4^{sq}	2.84	0.1223	-29.5890	0.0158	0.0
Li_4^{eq}	2.65	0.1609	-29.5921	0.0165	0.0
Li_4^{mal}	2.73	0.1601	-29.5937	0.0169	0.037
Li_4^{lin}	$R=2.734$ $r=2.631$	0.1617	-29.5897	0.0159	0.0
Li_4^{obl}	3.23	0.1221	-29.5827	0.0142	0.0
Li_4^{T}	2.70	0.1489	-29.6021	0.0190	4.72
Li_4^{rho}	2.57	0.1716	-29.6048	0.0197	0.0
$\text{Li}_4^{\text{para}}$	$R_1=R_2=3.05$ $\alpha=50.4^\circ$	0.1648	-29.6114	0.0214	0.045

Table 2. Ionization potentials for Li_n clusters

Cluster	First Ionization Potential	Second Ionization Potential
Li_2	0.1799	2.4258
Li_3^{tri}	0.1237	0.3633
Li_3^{eq}	0.1591	0.3357
Li_3^{iso}	0.1292	0.3619
Li_4^{tet}	0.1127	0.2192
Li_4^{tri}	0.1435	0.2247
Li_4^{sq}	0.1380	0.2305
Li_4^{eq}	0.1688	0.2070
Li_4^{mol}	0.1682	0.2051
Li_4^{lin}	0.1695	0.2063
Li_4^{obl}	0.1388	0.2284
Li_4^{T}	0.1501	0.2229
Li_4^{rho}	0.1600	0.2165
$\text{Li}_4^{\text{para}}$	0.1563	0.2184

END

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